

ARENECHROMIUM COMPLEXES IN COAL

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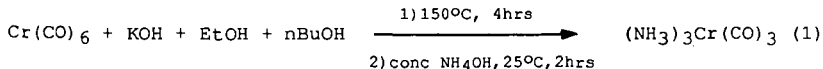
Introduction

When an arene is coordinated to $\text{Cr}(\text{CO})_3$, profound changes in its reactivity occur^{1,2}. Ring and benzylic hydrogen atoms exhibit enhanced acidity, and typical arene reactions such as electrophilic aromatic substitutions are quenched. In contrast, the ring carbon atoms are activated toward attack by nucleophiles¹. These changes in reactivity are manifestations of the forceful electron withdrawing nature of the $\text{Cr}(\text{CO})_3$ component, and of the ability of this group to stabilize charged intermediates. In addition, arenechromium tricarbonyl complexes have been proven to be good catalysts in the hydrogenation of dienes³. While most simple complexes such as toluenechromium tricarbonyl require the use of high temperatures and dihydrogen pressures, arenechromium tricarbonyl complexes with naphthalene, anthracene, and phenanthrene show remarkable activity under extremely mild conditions. Coal arenechromium tricarbonyl complexes may prove to be good internal hydrogenation catalysts for the hydrogenation of surrounding molecules.

Results and Discussion.

Experiments were carried out with a coal liquid in this exploratory investigation to avoid solubility problems inherent in the use of solid coals. The coal liquid used was distilled at approximately 850°C from run 250D at the Wilsonville pilot plant with Illinois No. 6 coal. In contrast to solid coals and heavy distillates, this material is soluble in all common organic solvents.

The first stage of research centered on the conversion of the aromatic hydrocarbons in the coal liquid into arenechromium tricarbonyl complexes. Reactions to form complexes with the coal liquid were carried out by a procedure for simple molecules in which the arene is refluxed in dioxane with chromium hexacarbonyl. However, this method required long reaction times and large excesses of chromium hexacarbonyl to achieve acceptable levels of complexation. To alleviate these problems, the use of an alternative reagent, triaminechromiumtricarbonyl, was investigated. This reagent is easy to synthesize⁵, equation 1, and has been used

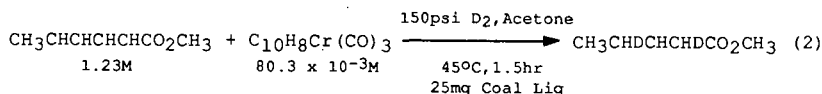


to obtain several organochromium complexes⁶. Reactions of the coal liquid with triaminechromiumtricarbonyl proved to be very successful. High yields of complexation with the coal liquid arene molecules were obtained. Indeed, the product was orange colored and crystalline in nature. The ¹³C NMR spectrum of one such product is shown in Figure 1. The carbonyl resonance appears at 234 ppm and

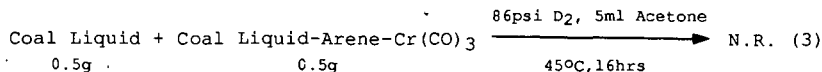
the aromatic carbon resonances shift to 80-100 ppm as anticipated.

The second stage of the investigation centers on hydrogenation transfer chemistry of the coal liquid arenechromium tricarbonyl complexes. Studies have been carried out with simple arenechromium tricarbonyl complexes^{1,7} as catalysts in the hydrogenation of methyl 2,4-hexadienoate in which the severity of reaction conditions varied from 150°C at 700 psi dihydrogen pressure for toluenechromium tricarbonyl to 27°C at 57 psi dihydrogen pressure for naphthalenechromium tricarbonyl. The dramatic increase in activity of the polycyclic arenechromium tricarbonyl complexes is that there are two long Cr-C bonds with the bridgehead carbon atoms that have bond orders less than one⁸. Thus, the longer and weaker bonds should be more easily displaced by the incoming diene ligand in the rate determining step. This advantage is not realized in the case of the monocyclic arenechromium tricarbonyl complexes such as benzenechromium tricarbonyl where all of the Cr-C bonds have equal length with bond orders close to unity. The effect of solvent was also examined. Coordinating solvents such as tetrahydrofuran or acetone increased the rate of the hydrogenation reaction presumably by facilitating the initial ligand substitution step.

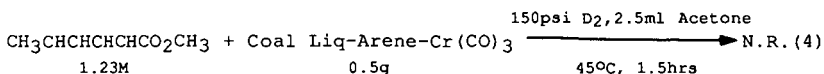
Hydrogenation reactions were carried out under mild conditions in a glass microhydrogenation apparatus at pressures lower than 200 psi and temperatures less than 50°C using dideuterium gas. The use of dideuterium allows the reduction step to be detected by means of deuterium NMR. A hydrogenation reaction was carried out with naphthalenechromium tricarbonyl to catalyze the hydrogenation of methyl 2,4-hexadienoate in the presence of small amount of coal liquid to test whether or not the coal liquid would poison the catalyst. This reaction, equation 2, proved to be successful with a



63% conversion of methyl 2,4-hexadienoate to methyl hex-3-enoate-2,5-d₂. It was evident that the presence of the coal liquid does nothing significant to inhibit the catalyst. The next set of experiments were carried out with the coal liquid arenechromium tricarbonyl complexed material. The coal liquid arenechromium tricarbonyl complexed material proved to be unsuccessful in catalyzing the hydrogenation of the surrounding molecules. In part, this could be due to the fact that all of the possible active sites for hydrogenation may of have been rendered unreactive by complexation with Cr(CO)₃. To test this line of reasoning, experiments were carried out on a mixture of the coal liquid arenechromium tricarbonyl complex and unreacted coal liquid as shown in equation 3. Analysis of the ²H NMR spectrum of the coal liquid arenechromium tricarbonyl reaction product showed that no significant deuteration had taken place.

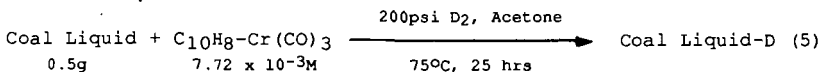


In order to clearly test the catalytic activity of the coal liquid arenechromium tricarbonyl complex, experiments were carried out with methyl 2,4-hexadienoate as the substrate and the coal liquid arenechromium tricarbonyl complex as the catalyst as shown in equation 4. The ^2H NMR of the reaction product showed the coal liquid and unreacted methyl 2,4-hexadienoate indicating no reaction.



Although the activity of the coal liquid arenechromium tricarbonyl complex as a hydrogenation catalyst appears to be small for methyl 2,4-hexadienoate as well as for unreacted coal liquids under the mild conditions employed, it may well prove to be viable under moderately more severe conditions. In addition, the nature of the aromatic rings in this particular coal liquid may actually lead to very inactive coal liquid arenechromium tricarbonyl complexes. A slightly heavier distillate may contain more polycyclic aromatic hydrocarbons and yield more active complexes while still affording the conveniences provided by the use of a coal liquid.

In order to test the hypothesis that hydrogenation substrates do not exist in the coal liquid, a reaction was carried out with naphthalenechromium tricarbonyl, an active catalyst, and unreacted coal liquid as the substrate, equation 5. A comparison of the ^2H



NMR spectra of the unreacted coal liquid before and after the reaction, Figure 2, shows that dideuterium addition has taken place. First, the relative aromatic deuterium content has decreased and the aliphatic deuterium content has increased. Second, the two major resonances of the unreacted coal liquid at approximately 1.54 ppm and 1.16 ppm are no longer the dominant resonances. Rather, the new dominant resonances in the reacted coal liquid are at approximately 2.27 ppm and 1.45 ppm. In addition, two other new signals have appeared at 3.57 ppm and 2.71 ppm. Thus, it can be concluded that hydrogenation of the coal liquid had occurred.

Conclusions

A synthetic method for the preparation of coal arene chromium tricarbonyl complexes has been established. The series of hydrogenation reactions with coal liquid arene chromium tricarbonyl complexes shows that there is nothing inherent in coal materials that poison the arenechromium tricarbonyl catalyst and that there are active sites in the coal liquid for hydrogenation. However, the actual arenechromium tricarbonyl complexes formed in the coal liquid are not active enough for extensive hydrogenation under the mild experimental conditions that we used. As mentioned before, monocyclic complexes require higher temperatures and pressures for hydrogenation than polycyclic complexes do. Research in this area is continuing to test the capacity of coal liquid arenechromium tricarbonyl complexes to catalyze dihydrogen addition.

Experimental

The coal liquid was obtained through Amoco Research Center from the Wilsonville Pilot Plant, Run 250D. The ^{13}C NMR spectra were recorded on a General Electric GN 300 operating at 300MHz. The ^2H NMR spectra were recorded on a Varian XL 1000 operating at 400MHz. The ^1H NMR spectra were recorded on the University of Chicago 500MHz spectrometer. Tetrahydrofuran, dibutyl ether, and dioxane were freshly distilled from sodium benzophenone ketyl immediately before use. Hexane was shaken with sulfuric acid prior to use. All solvents were deoxygenated by means of standard freeze-pump-thaw methods. Potassium hydroxide, acetone, and chromium hexacarbonyl were used as received.

Triaminechromium tricarbonyl

Chromium hexacarbonyl (17.6g, 0.08mol), potassium hydroxide (32.0g), ethanol (80ml), n-butanol (80ml) and water (25ml) were placed in a flame dried three neck flask fitted with a stirrer and a reflux condenser. The reaction flask was placed in an oil bath which was warmed gradually to 150°C. Chromium hexacarbonyl, which sublimed initially, was washed out later by the solvent and no more sublimation took place. The reaction solution gradually turned red. After 4h at reflux, the mixture was collected, 150mL of concentrated aqueous ammonia solution was added and the mixture was slowly stirred for two hours. A yellow precipitate was collected on a glass filter, washed with aqueous ammonia and ether.

Coal liquid arenechromium tricarbonyl

Triaminechromium tricarbonyl (4.68g, 0.025mol), coal liquid (5g), and dioxane (25mLs) were loaded into a 100 mL flask provided with a magnetic stirrer, and a reflux condenser. The solution was refluxed on an oil bath for 48 hrs. The reaction mixture was filtered through Celite in a glass filter and the flask and Celite were washed with ether. The product was purified over a column of silica gel with a 1:1:4 chloroform : dichloromethane : hexane.

Napthalenechromium tricarbonyl

Napthalenechromium tricarbonyl was prepared by a slightly modified procedure¹⁰ to that described by Pauson⁴. A mixture of napthalene (5.3g, 0.042mol) and chromium hexacarbonyl (4.4g, 0.020mol) were refluxed in dibutyl ether (100 mL), hexane (10mL), and tetrahydrofuran (1mL) for 70 hrs. The heating bath was maintained at 160°C for 15 hrs and at 145°C for the remaining time. Solvent and excess napthalene were removed under vacuum and the product purified on a column of silica gel with a 1:1:4 chloroform : dichloromethane : hexane.

Hydrogenation reactions

Hydrogenation reactions were carried out on a 10mL micro hydrogenation apparatus. Typically, the reactants and dried, deoxygenated acetone were placed in the reactor and it was evacuated and flushed with dinitrogen three times, dideuterium three times and then brought up to the final dideuterium pressure at the desired temperature. After the reaction time, the mixture was filtered through Celite in a glass filter and concentrated under vacuum.

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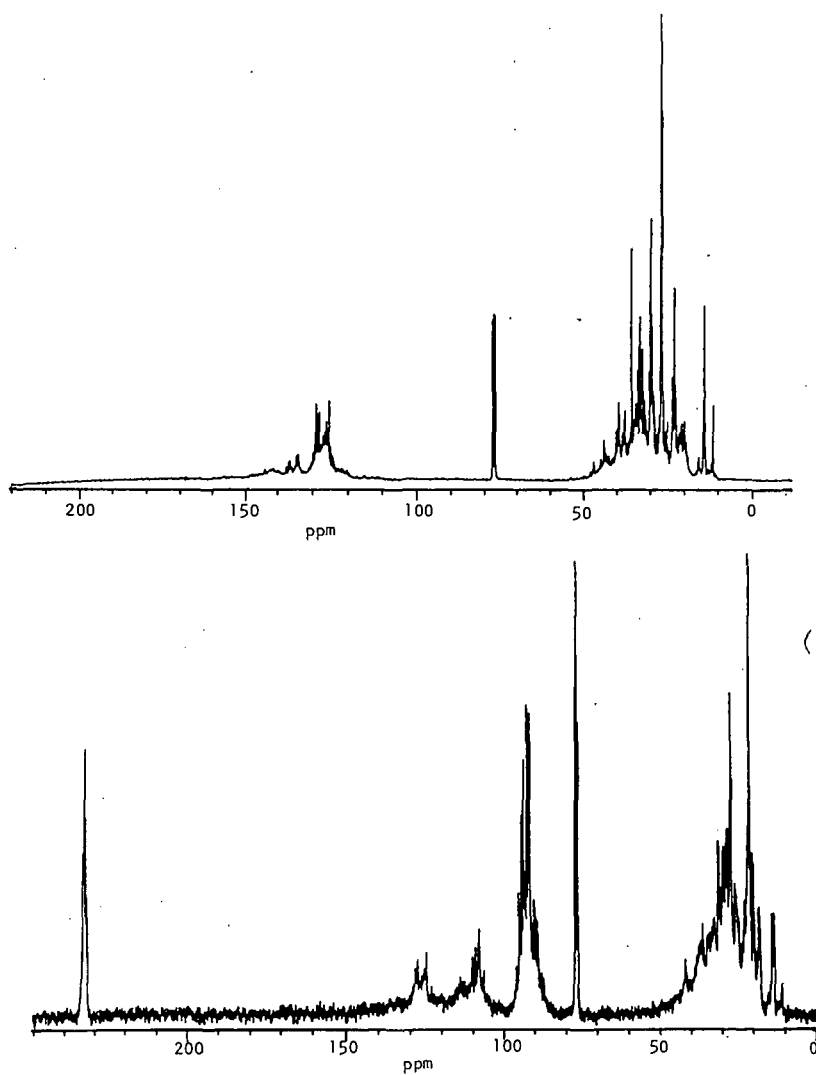


Figure 1. (a) ^{13}C NMR Spectrum Of Wilsonville Coal Liquids in CHCl_3 .
(b) ^{13}C NMR Spectrum Of Coal Liquid Arene- $\text{Cr}(\text{CO})_3$ in CHCl_3

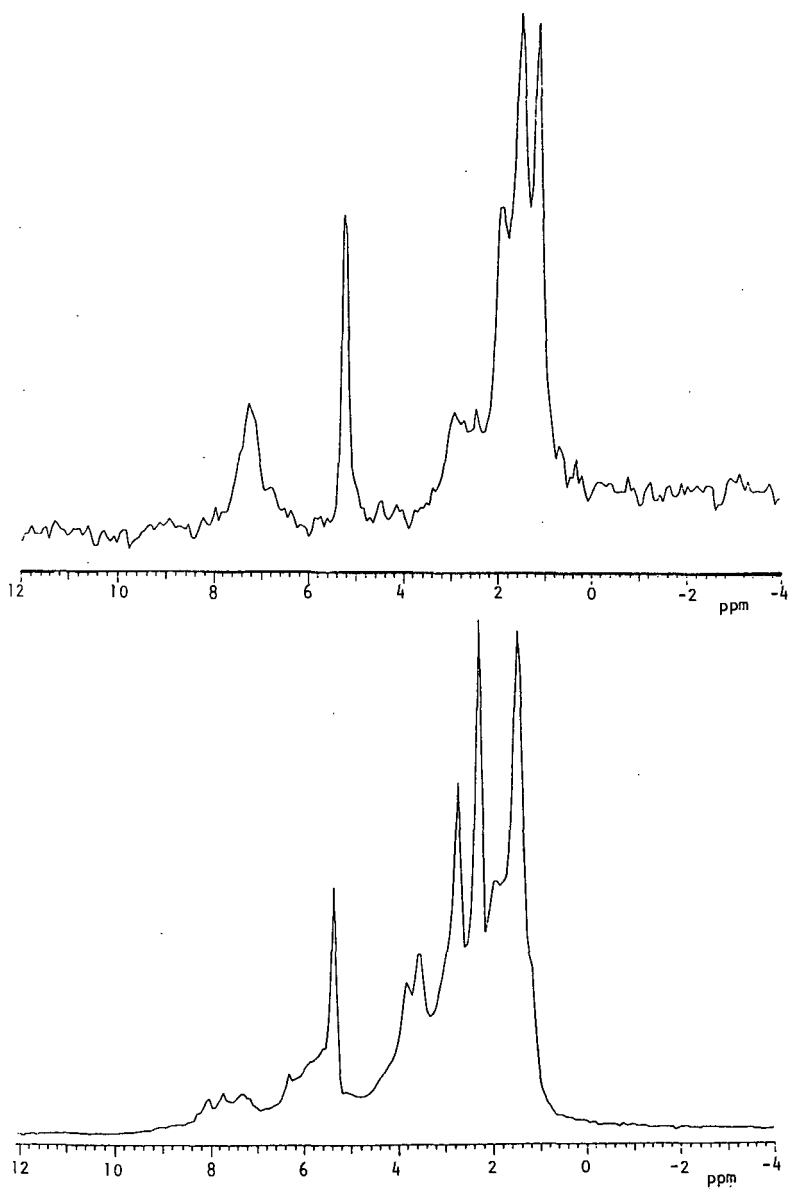


Figure 2. (a) ^2H NMR Spectrum of Unreacted Coal Liquid in CH_2Cl_2
(b) ^2H NMR Spectrum of Equation 6 Product in CH_2Cl_2 .